

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

**Structural Reconstruction and Spontaneous Formation of Fe
Polynuclears: A Self-Assembly of Fe-Porphyrin Coordination Chains
on Au(111) Revealed by Scanning Tunneling Microscopy**

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1. STM results of the TPyP on a clean Au(111) surface.

The deposition of TPyP molecules, on a clean Au(111) surface held at room temperature, leads to a close-packed monolayer formation (Figure S1a).^{1,2} A close inspection (Figure S1b) reveals a “double-row” structure, where the molecules are oriented the same way within every second rows.¹ The unit cell of the structure is indicated in Figure S1b, and its parameters are as follows: $a = 1.36 \pm 0.05$ nm, $b = 2.63 \pm 0.05$ nm, and $\theta = 95 \pm 2^\circ$. Defects appearing as stripes of vacancies are indicated by the arrow in Figure S1b.²

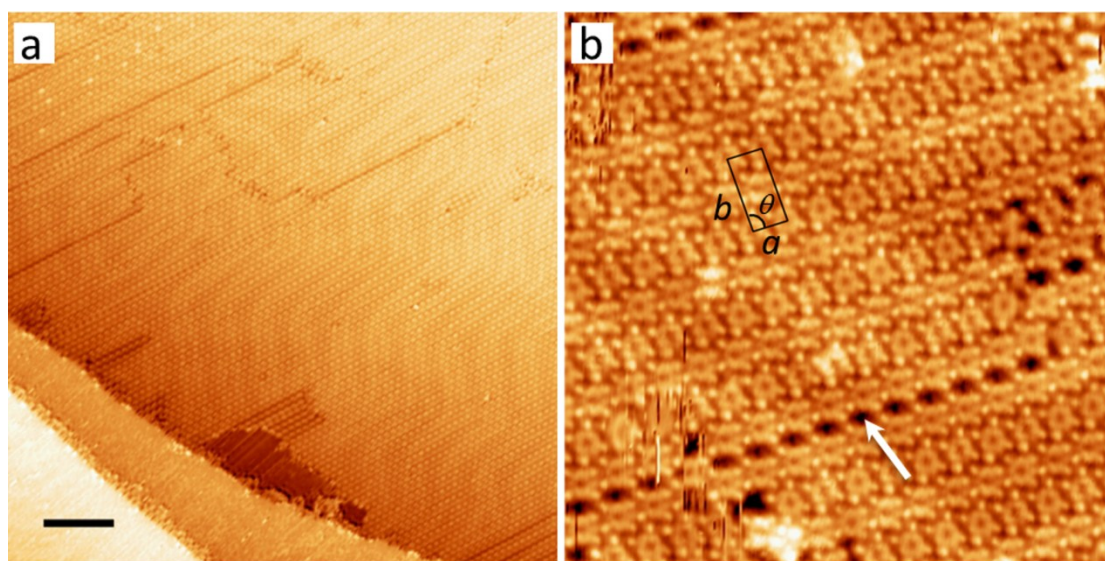


Figure S1. STM overview (scale bar: 20 nm) (a) and a close inspection (19 nm \times 19 nm) (b) of the TPyP close-packed monolayer. Data acquisition conditions: (a) $U = -1.2$ V, $I = 0.1$ nA; (b) $U = -1.2$ V, $I = 50$ pA.

- 1 W. Auwärter, A. Weber-Bargioni, A. Riemann, A. Schiffrin, O. Groning, R. Fasel and J. V. Barth, *J. Chem. Phys.*, 2006, **124**, 194708.
- 2 J. P. Hill, Y. Xie, M. Akada, Y. Wakayama, L. K. Shrestha, Q. Ji and K. Ariga, *Langmuir*, 2013, **29**, 7291.

2. The orientation and the length distribution of the chains.

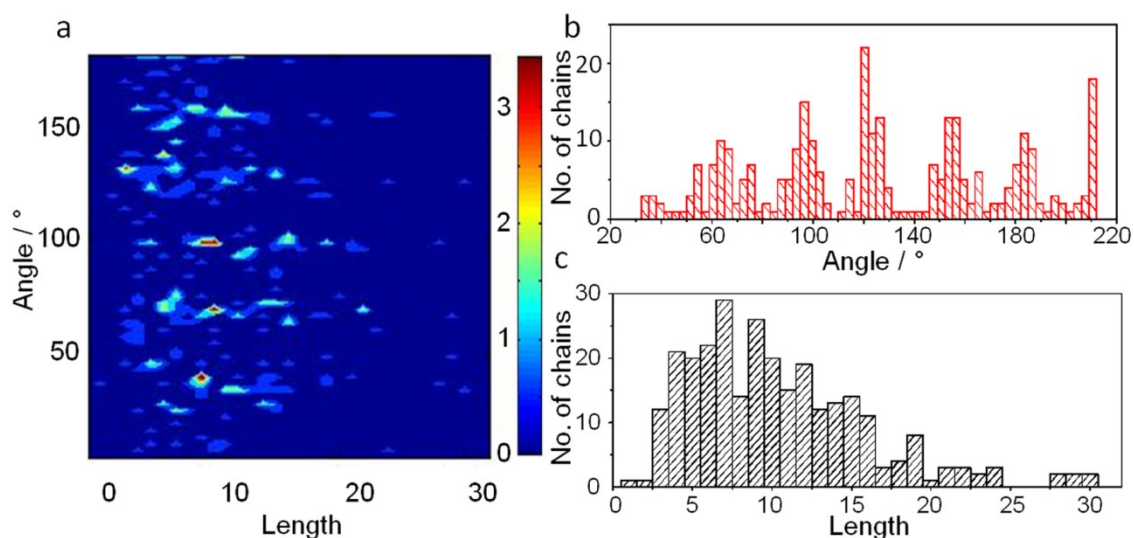


Figure S2. (a) The number of the chains as a function of the angle and the length of a chain. x / y - coordinate refers to the length/angle of a chain. The “spectrum” bar defines the number of chains. The total number of molecules counted is ~ 3000 . (b) The number of chains as a function of the angle of a chain. (c) The number of the chains as a function of the length of a chain. In (a) and (c), the length of a chain is represented by the number of molecules within the chain. In (a) and (b), the angle of zero refers to that the orientation of the chain is parallel to the fast scan direction of the STM image.

3. Size of the “bright dots”.

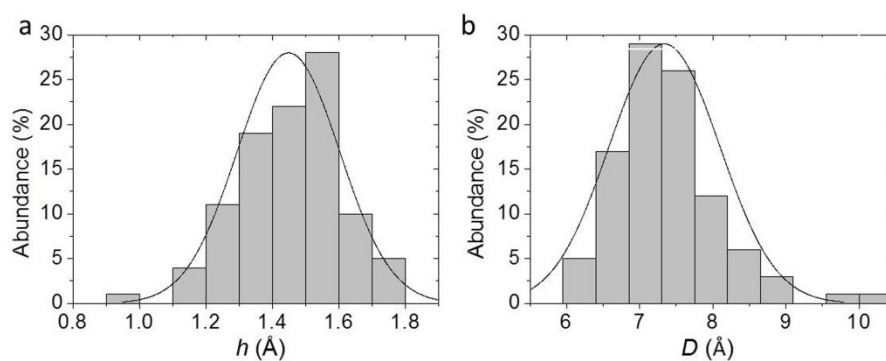


Figure S3. Distributions of the apparent height (h) (a) and the diameter (D) of the “bright” dots (i.e. d -Fe) (the diameter is defined as the full-width-at-half-maximum (FWHM) of the line profiles across a dot). Normal distribution fitting curves overlaid show the mean value of the apparent height is 1.4 ± 0.2 Å, and the diameter is 7.3 ± 0.8 Å. The number of “bright” dots counted is ~ 100 .

4. STM overviews of the sample covered by Fe.

We have deposited Fe on a clean Au(111) surface using a constant deposition rate. The Fe coverage (Θ_{Fe}) was determined by STM images acquired at room temperature. To minimize both the effect of the tip artifact and the Fe lattice gas, we have prepared a sample with a high Fe coverage by using a deposition duration of 100 sec (Figure S4a shows a typical STM image), which results in a Θ_{Fe} of $(3.0 \pm 0.4) \times 10^{-1}$ ML. Therefore the deposition rate was ~ 0.18 ML/min. The sample with $\Theta_{Fe} = \sim 3.0 \times 10^{-2}$ ML was obtained by a 10 sec – deposition (Figure S4b).

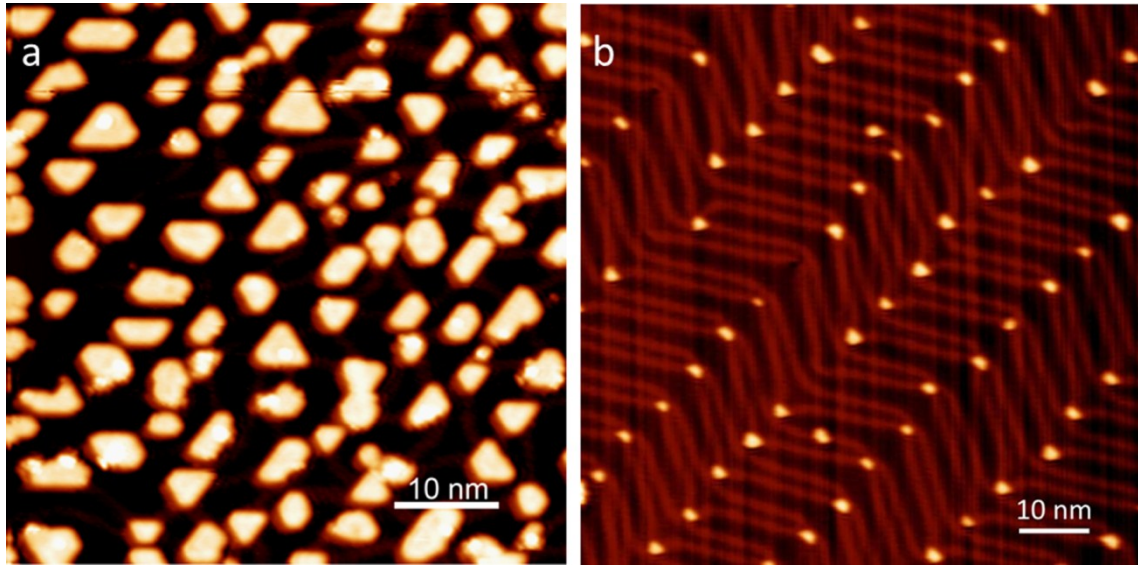


Figure S4. STM overviews of the sample covered by Fe. Fe atoms form islands at the elbows of the herringbone reconstruction structures. (a) $\Theta_{Fe} = (3.0 \pm 0.4) \times 10^{-1}$ ML; $U = -1.2$ V, $I = 200$ pA. (b) $\Theta_{Fe} = \sim 3.0 \times 10^{-2}$ ML; $U = -1.2$ V, $I = 80$ pA.